

Ferrate(VI) as a Possible Oxidant on the Martian Surface

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1. Introduction

Viking "Biological" experiments (Oyama et al. 1976, Levin & Straat 1977) revealed an unexpected chemical activity in the surface material, which in some ways resembled biology but was ultimately explained by a rather complex chemistry. It was shown, in these experiments that moisturizing Martian soil resulted in oxygen evolution, while addition of a bacterial nutrient solution (^{14}C - formate, glycine, lactate, etc.) released $^{14}\text{CO}_2$, along with some oxygen. These observations indicated the presence of a strong oxidant on Martian surface, or, most probably, several different oxidants (Klein 1978). The nature of the oxidants in Mars soil, and their distribution, are important for choosing Martian landing sites. Iron as an one of the most abundant elements in Martian soil, deserves attention in this context, since it has a whole set of oxidation states, from 0 to +6, even though in terrestrial conditions only Fe(0), Fe(+2) and Fe(+3) are commonly found. Fe(+4, +5) are unstable, but Fe(+6) has been characterized in some detail. Though it was never identified as a natural compound on the Earth, it is stable enough under some conditions (highly alkaline solutions, lack of reductants, dry atmosphere, low temperature) that are not normally encountered in the terrestrial environment, but still can be considered as a possibility in Martian soil. Here are discussed ferrate(VI) formation and accumulation in Martian soil, and experimental data are presented on the spectral characterization and chemical behavior under conditions simulating the Viking "biological experiments".

2. Experimental materials and methods.

Crystalline potassium ferrate, K_2FeO_4 , was prepared essentially as outlined previously (Thompson et al. 1951, DeLaude & Lazslo 1966). Iron(III) nitrate was oxidized by a concentrated solution of sodium, or potassium hypochlorite. The mixture turns dark purple as ferrate forms. Potassium, or barium ferrate was

then precipitated from that solution by pouring it in the saturated KOH or adding solid $\text{Ba}(\text{OH})_2$ to it. Stability of K_2FeO_4 crucially depends on water removal. BaFeO_4 was less sensitive to moisture.

UV-Visible absorption spectra of were recorded using diode array HP 8453 instrument, reflectance spectra measured on Beckman 5240 and Pima (Integrated Electronics) instruments. Mössbauer spectra were obtained at 300K in zero magnetic field using a constant acceleration Ranger Scientific spectrometer, with isomer shifts taken against iron metal at 22°C. X-Ray absorption near edge structure (XANES) spectra were obtained in Argonne National Laboratory synchrotron facility.

Gases released in the reactions of ferrate(VI) with ordinary water and H_2^{18}O , and with aqueous solutions of organic compounds, were analyzed, first, using Micro-Oxymax respirometer (Columbus Instruments) designed to detect low levels of oxygen and/or carbon dioxide production/consumption, and, second, with Varian Saturn 2000 GC-MS instrument with helium as a carrier gas.

3. Results and discussion

The following basic questions have been addressed in this study:

1. Is there an opportunity to form ferrate (VI) on Mars, according to what is presently known about its surface composition and environmental conditions?
2. Would such a compound persist and accumulate under those conditions?
3. Would it be able to display essential reactivity that was found in the samples of Martian soil in Viking experiments, i.e. to produce oxygen gas while moisturized, and
4. Would it produce carbon dioxide while contacting with organic materials that constituted nutrient solution in those experiments?
5. Would these chemical activities be impaired at heating in a way similar to such an inactivation in Viking's experiments?
6. Having in mind Mars exploration programs, what are the possible approaches for identification of $\text{Fe}(\text{VI})$, and in particular what are its spectral that permit its characterization by both contact measurements and remote sensing?

On the Formation and Persistence of Ferrate(VI) in Martian Soil.

On one hand, $\text{Fe}(\text{VI})$ was formed in the reactions of iron-containing materials with some peroxides (Kisilev et al. 1989, Dedushenko et al. 1997). On the other hand, there is a strong belief that active oxygen species, such as peroxides, superoxides, hydroxyl radicals, form under UV irradiation in Martian atmosphere, and affect its soil (Huguenin et al. 1979, Huntten 1979) Overall, Martian atmosphere is highly oxidized, with domination of carbon dioxide and presence of some dioxygen. In these circumstances, ferrate(VI) can serve as a form of

stabilization and storage of active oxygen, if however its decomposition is slow enough to permit its accumulation.

Ferrate(VI) is rather stable at $\text{pH} > 9$ only, and even in these solutions it is readily reduced by most of organic materials. At lower pH, not only organic materials, but water is oxidized, too. So, thermodynamically, highly alkaline environment is needed in order Fe(VI) to be stored. This requirement is not so limiting for Mars soil, as it could seem on the first glance. Indeed, there are strong reasons to assume that both pre-Cambrian Earth and Mars at some stage of their geological history were covered with alkaline "soda ocean" (Kempe & Degens 1985, Mills & Sims 1995).

Ferrates of alkaline metals are rather unstable in the presence of moisture. However Martian surface is extremely dry and cold. Thus, even alkaline ferrates can be stabilized there. Besides, other ferrates, such as those of calcium or barium, are much less water soluble and at the same time more stable in humid milieu. Essential is that Fe(VI) is not sensitive to light. Therefore, there is enough reason to suggest that the formation of Fe(VI) and its preservation in soil are consistent with the present knowledge of the chemical composition and environmental conditions on the Martian surface.

Spectral Characterization.

Dark purple color of ferrate(VI) is due to its absorption spectrum, with a peak at 507 nm. This spectrum makes Fe(VI) very distinct from other forms of dissolved iron, and absorption spectrum is an appropriate tool for Fe(VI) identification. With Mars exploration in mind, more practical seem reflectance spectra that can be recorded by remote sensing. The band at 1.6 μm is a characteristic one, in ferrate(VI) reflectance spectrum, and it can be used as a marker to search for the presence of Fe(VI) on the Martian surface.

Mössbauer spectroscopy is the most powerful approach to the identification of iron oxidation states. It is especially important in the context of these studies since a compact Mössbauer instrument has been developed for the future Mars '01 and '03 missions. Mössbauer spectrum of a sample containing potassium ferrate(VI), together with other iron species is a superposition of two main spectral components. The singlet line with a negative isomer shift of -0.91 mm/s is identified as the primary Fe(VI) phase. A negligible quadrupole splitting is expected for Fe(VI) in K_2FeO_4 based on its $3d^2$ electronic configuration in a tetrahedrally coordinated site.

XANES spectra of Fe(VI) are especially sensitive to the oxidation state and geometry of the closest and second coordination sphere of the excited atom. Significant differences in the structure of XANES spectra of ferrate(VI) and of Fe(III) or Fe(II) compounds have been found in both solutions and crystalline samples. Method is quite sensitive, permitting to reveal the presence of iron in a given oxidation state at the level of 10 ppm, thus making its promising for fingerprinting the presence of Fe(VI) in the samples brought from Mars.

Ferrate(VI) Reactivity.

In the Viking gas exchange experiments, it was found that Martian soil released O_2 in the amounts of 70 to 700 nmol /mL upon introduction of water into the sample (Oyama et al. 1976). O_2 was released also from a sample of soil that

had been pre-heated at 145° C, even though the amount of gas was substantially reduced.

Dry ferrate is not immediately reactive with such aprotic solvents as ether, chloroform, benzene, which permits their application for removal of traces of water from ferrate preparation at the final stage of its purification. Neither is ferrate(VI) soluble in any of those solvents. Upon addition of water to potassium ferrate, bubbling indicates gas evolution. GC-MS analysis of gas product after the reaction with H₂¹⁸O revealed that the gas product formed in the head space of reactor vessel was indeed ¹⁸O₂, i.e. the process is a true water oxidation, not a ferrate decomposition catalyzed by water, and that there is no fast oxygen exchange between ferrate anions and water. Preheating of potassium ferrate(VI) inhibited oxygen evolution.

In the Viking Labeled Release Experiment ¹⁴CO₂ was rapidly released upon contact of the surface material with ¹⁴C labeled nutrient solution. The reaction slowed down after a small fraction of the added organic medium decomposed. Preheating the samples up to 160°C for three hours completely inhibited the release of ¹⁴CO₂ (Levin & Straat 1977).

Extremely strong oxidizing power of Fe(VI) was well documented in its reactions with a number of various compounds in the presence of water (see e.g. (Delaude & Laszlo 1996)). In our experiments, addition of aqueous solutions of formate and/or lactate to powdered potassium ferrate(VI) resulted in the release of CO₂. At the same time, some dioxygen was formed, apparently due to a concomitant reaction with water. Preheating ferrate considerably inhibited CO₂ evolution. All these observations are in line with the results of Viking Labeled Release Experiments.

To summarize, ferrate(VI) looks a likely candidate for the Martian soil oxidant, and it seems the forthcoming Mars missions will be able to test this hypothesis, using both in situ measurements, and analysis of returned samples.

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